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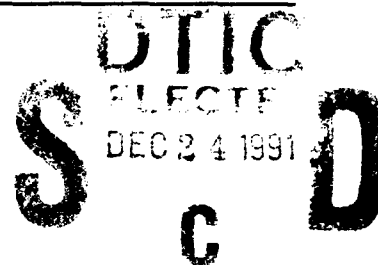
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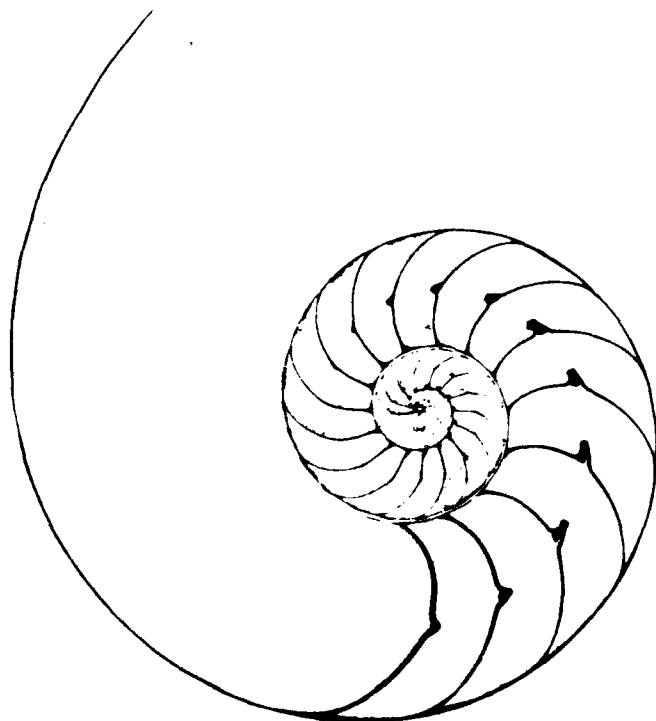
**Workshop
on the**

Design and Processing of Materials by Biomimicking

**Seattle, Washington
April 2-4, 1991**



***Air Force Office of Scientific Research
and the University of Washington***



91-18895



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- 3 An international workshop entitled "Design and Processing of Materials by Biomimicking" was held in Seattle, WA on 2-4 April 1991. Seventy national and international researchers with multidisciplinary interests participated in the workshop at which fifteen invited speakers gave presentations. Sessions were held on the following topics: Mechanisms and Control of Nucleation and Growth in Biomineralization; Processing and Properties of Synthetic Materials through Biomimicking; and Identification of Critical Issues and Future Directions in Biomimicking. Periods of questions and discussions were held after each talk and at the conclusion of the talks. The proceedings of the workshop, including formal manuscripts of the invited presentations and transcripts of the subsequent discussions, will be published in book form in early 1992 under the same title as the workshop.

WORKSHOP ON THE DESIGN AND PROCESSING OF MATERIALS BY BIOMIMICKING

April 2-4, 1991

**Battelle Conference Center
4000 N.E. 41st Street
Seattle, Washington**



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*Organized by
Mehmet Sarikaya and Ilhan A. Aksay*

*Sponsored By
The U.S. Air Force Office of Scientific Research
and
The University of Washington*

Tuesday April 2

Registration and Breakfast, 7:00 - 8:00 a.m.
Battelle Conference Center

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Session I 8:00 - noon

A. General Discussion of AFOSR Programs

Moderator: Mehmet Sarikaya

1. **Biomimetics: Natural Materials as Paradigms for Superior Aerospace Systems**
Frederick L. Hedberg and George K. Haritos 1

B. Structures and Properties of Biological Composite Systems

Moderator: Ilhan A. Aksay

2. **Microstructure of an Insect Cuticle and Its Applications to Advanced Composites**
Stephen L. Gunderson and Rebecca C. Schiavone 2

Coffee Break

3. **Hierarchical Twin Structures and Multiple Tilings in the Nacre of Abalone Shell**
Mehmet Sarikaya, Jun Liu, and Ilhan A. Aksay 3
4. **The Functions of Biocomposites**
Stephen A. Wainwright 4

Lunch, Battelle Conference Center

Session II 1:00 - 5:00 p.m.

C. Structures and Properties of Biological Composite Systems

Moderator: George K. Haritos

5. **Microstructure-Property Relations in Vertebrate Hard Tissues: Microdamage and Toughness**
John D. Currey 5
6. **Structures and Properties of Biological Materials**
Georgio Jeronimidis and Julian F. V. Vincent 6

Coffee Break

D. Structures and Properties of Biological Polymers

Moderator: James T. Staley

7. **Role of Molecular Genetics in Polymer Materials Science**
Maurille J. Fournier, Thomas L. Mason, and David A. Tirrell 7
8. **Molecular Design of Spider's Silks**
John M. Gosline, Cynthia Nichols, and Paul Guerette 8

Dinner, Battelle Conference Center

Session III 8:00 - 10:00 p.m.

E. Evening Discussions

Wednesday April 3

Breakfast, 7:00 - 8:00 a.m., Battelle Conference Center

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Session IV

8:00 - noon

F. Mechanisms and Control of Nucleation and Growth in Biomineralization

Moderator: Frederick L. Hedberg

9. **Biomineralization, the Inorganic-Organic Interface and Crystal Engineering**
Stephen Mann, Brigid R. Heywood, Jon M. Didymus, Fiona C. Meldrum, Sundara Rajam,
and Vanessa J. Wade 9
- 10A. **Crystal Organization in Rat Bone Lamellae**
Stephen Weiner and Wolfie Traub 10
- 10B. **Composite Materials of Single Crystals and Proteins:
Comparison between Mollusk Prismatic Layer and Sea Urchin Skeletons**
Amir Berman, Lia Addadi, and Stephen Weiner 11

Coffee Break

11. **Ultrafine Inorganic Particle Formation in Bacteria**
Richard B. Frankel 12
12. **Size-Quantized Particles at Artificial Membrane Interfaces**
Xiao K. Zhao and Janos H. Fendler 13

Lunch, Battelle Conference Center

Session V

1:00 - 5:00 p.m.

G. Processing and Properties of Synthetic Materials through Biomimicking

Moderator: Rebecca C. Schiavone

13. **Hierarchical Structures of Soft Connective Tissues--
Relationships to Properties and Function**
Eric Baer, James J. Cassidy, and Anne Hiltner 14
14. **Thin Film Biomimetic Composites and Ceramics**
Paul Calvert and Jeremy Burdon 15

Coffee Break

15. **Processing of Ceramics by Biomimicking**
Ilhan A. Aksay, James T. Staley, and Mehmet Sarikaya 16

Dinner, Ivar's Salmon House, Seattle

**Thursday
April 4**

Breakfast, 7:00 - 8:00 a.m., Battelle Conference Center

**Session VI
8:00 - noon**

**H. Identification of Critical Issues and Future Directions
in Biomimicking**

Moderators: Ilhan A. Aksay, George K. Haritos, Frederick L. Hedberg,
Mehmet Sarikaya, and Rebecca C. Schiavone

Coffee Break

I. Procedures for Grant Applications to the AFOSR

Moderator: Mehmet Sarikaya

Speakers: Frederick L. Hedberg and George K. Haritos

CLOSING REMARKS

Noon END OF WORKSHOP AND LUNCH

Preface

This workshop on the "Design and Processing of Materials by Biomimicking," sponsored by the U.S. Air Force Office of Scientific Research and the Advanced Ceramics Materials Laboratory of the Washington Technology Center at the University of Washington, has been organized to provide an opportunity for researchers working with biomimicking concepts and techniques in widely diverse fields to exchange information and ideas that will stimulate the development of new synthetic materials. Based on the premise that progress in this endeavor can only result from strong collaboration among researchers of diverse disciplines, key speakers representing the fields of biology, zoology, botany, chemistry, physics, applied mathematics, and materials science and engineering as well as selected participants who are active in biomimicking-related research have been invited to this workshop from government agencies, industry, and universities.

Biomimicking is now regarded as an area of research in which the analysis of natural materials will provide insights into the design of novel manmade materials, resulting in superior structures able to withstand the requirements placed upon advanced materials. It is well recognized that biological systems efficiently produce complex composites possessing unique properties with greater control than is possible with synthetic materials. Biological materials often have hierarchical structures with unprecedented properties at spatial levels on the molecular, micrometer, and macrometer scales. The dynamism of these systems allows the collection and transport of constituents; the nucleation, configuration, and growth of new structures by self-assembly; and the repair and replacement of old or damaged components. With this in mind, this workshop is intended to identify the most critical issues and to establish future directions for biomimicking in materials science and engineering.

Three primary areas to be discussed are: (i) structures and properties of biological systems, (ii) mechanisms and control of nucleation and growth in biomineralization, and (iii) processing and properties of synthetic materials produced through biomimicking. The primary biomaterials of interest include structural components such as inorganic/organic composites (e.g., seashell and bone); all-organic composites (e.g., insect cuticles), all-ceramic components (e.g., sea urchin skeletal units), and inorganic ultrafine particles (e.g., magnetite).

The workshop has been designed to encourage informal yet extensive discussions on the outstanding points of each presentation in order to establish the critical problems and directions for future research. It is hoped that the participants at the workshop will actively participate in the discussions.

A proceedings of the workshop is planned in order to provide a permanent record of the new information generated by the workshop. The proceedings will include final papers by the invited speakers and the edited transcripts of the discussions that follow each paper. The proceedings is intended to be a guideline for researchers in the field of biomimicking.

M. Sarikaya

I. A. Aksay

A-1

BIOMIMETICS: NATURAL MATERIALS AS PARADIGMS FOR SUPERIOR AEROSPACE SYSTEMS

Frederick L. Hedberg and George K. Haritos

**Air Force Office of Scientific Research
Bolling AFB, Washington D.C. 20332-6448 USA**

The Air Force basic research community has defined a new research thrust to explore the possibility of developing superior aerospace materials and systems through a better understanding of naturally evolved systems. "Biomimetics" is now a funded AFOSR research initiative, jointly pursued by the Chemical and Atmospheric Sciences and the Aerospace Sciences Directorates. This workshop is organized on the premise that progress in this endeavor can only result from strong collaboration among investigators from widely diverse fields of traditional disciplines, including biology, zoology, botany, chemistry, physics, processing and materials sciences, applied mathematics, and mechanics. Thus motivated, we intend for the workshop to plant the seeds for such cooperation by bringing together noted representatives from these fields of research. The goals of this workshop are to further educate the Air Force participants in the possibilities of biomimetic design and processing and to encourage the research participants to address the interfacing of these possibilities with aerospace needs. Natural materials cannot be used for many aerospace applications because of their chemical instability at the temperatures associated with their use. For instance, projected airframe temperatures are as high as 1000° C at hypersonic speeds, and uncooled turbine engine component temperatures can surpass 1500° C. The analysis of natural structural design, however, may offer us insight into novel designs for manmade structures which afford significantly improved mechanical properties but are fabricated from synthetic materials based upon temperature-resistant chemistry. Similarly an understanding of the mechanism of growth of inorganic crystals in nature may reveal new processes for obtaining the nanostructure required for improved ceramics and for advanced ceramic, electronic, or electrooptical applications. These processes may then be replicated using precursors for advanced ceramic, electronic, or electrooptical materials. Complex composite structures consisting of both inorganic and organic materials and having potential for a variety of aerospace applications may even be tailored for use and "grown" if we can eventually understand and mimic the comprehensive natural process referred to as "self-assembly."

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MICROSTRUCTURE OF AN INSECT CUTICLE AND ITS APPLICATIONS TO ADVANCED COMPOSITES

Stephen L. Gunderson and Rebecca C. Schiavone

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Advanced composites have increased in popularity as structural materials over the last few decades, replacing their heavier and more brittle counterparts. However, improvements in the performance characteristics of advanced composite materials are required to meet the everchanging and demanding criteria of new and future applications. Characteristics such as specific strength, specific stiffness, and damage tolerance are some of the areas in need of enhancement. Through the analysis of natural composite materials and structures and by applying their novel design characteristics to synthetic systems (biomimetics), some or all of these challenges may be met. The bessbeetle cuticle is an excellent example of one such natural composite that possesses some unique designs which may contribute to the development of improved manmade composite materials and structures. The bessbeetle cuticle or exoskeleton is a natural polymeric structural composite that is lightweight, strong, stiff, and suprisingly damage tolerant. The microstructure, which is strikingly similar to its synthetic analogue, consists of chitin fibers embedded in a proteinacious matrix. Some of the novel designs associated with the bessbeetle cuticle which could be applicable to manmade composites include its structural hierarchy, fiber and matrix characteristics, constituent organization, and the methods by which it deals with stress concentrations.

A related area of materials research is smart technologies. Smart technologies involve using sensors in a material or structure to retrieve processing information, monitor the health of the structure, and improve performance characteristics. Animals are innately composed of smart materials and structures to help collect and process information in real-time on the animals' well being or health. For example, pain, thirst, hunger, temperature, position of body parts, rate and direction of movement, blood pressure, pH balance, and levels of oxygen and carbon dioxide are just some of the information that is constantly monitored. At the same time, the animal is also processing information about its environment through visual, auditory, tactile, olfactory, and gustatory senses. The diversity of nature has produced many unique systems which help an organism survive under special conditions or in a specific niche. Studying these systems could assist in smart technology research and the production of synthetic smart materials.

HIERARCHICAL TWIN STRUCTURES AND MULTIPLE TILINGS IN THE NACRE OF ABALONE SHELL

Mehmet Sarikaya, Jun Liu, and Ilhan A. Aksay

Department of Materials Science and Engineering
Advanced Materials Technology Center, Washinton Technology Center,
University of Washington, Seattle, WA 98195 USA

The superior physical properties of biocomposites over those of synthetic materials have been attributed to their unique structural organization of the component phases. Through *biomimetic* approaches, it may be possible to manufacture new composites, such as cermets and cerpolys, with microarchitectures similar to biocomposites in order to achieve properties that will satisfy the demands for technological advancements not yet possible by current processing techniques. One of the keys to the success of any *biomimetic* approach is the understanding of the structures of biocomposites and the interrelationships between hard and soft tissues, at all levels of spatial resolution. The current work has been undertaken to study the detailed structure of the nacre of red abalone shell since this biocomposite has been shown to have excellent mechanical properties and, yet, has a relatively simple microarchitecture.

The nacre has the form of a "brick and mortar" microarchitecture with 0.5- μm -thick aragonite platelets and a 20-nm-thick organic matrix between them. An analysis performed by transmission electron microscopy imaging and diffraction has revealed that, in the face-on configuration, the structure can be described by twinning on three different length scales: (i) first generation, incoherent twinning between platelets; (ii) second generation, coherent twinning between domains within platelets; and (iii) the third generation, nanoscale twins within domains. Both 60° and 90°-twin boundaries were observed at different length scales, a phenomenon which has never been encountered in natural mineral aragonite. The structures of biological soft tissues, such as tendon, are known to be hierarchical. To our knowledge, this is the first time that an inorganic component of a biological material has been shown to have a hierarchical structure. In this case, the hierarchical twin structure covers a length scale in six orders of magnitude, from the nanometer to millimeter scale.

Further studies indicate that aragonite platelets could be regarded as space filling tiles at each layer. Since each tile, i.e., a platelet, is twin related with the neighboring one on the same layer, this suggests that the underlying organic matrix must have a superstructure that perfectly fits all variants of twins in both 60° and 90°-symmetry platelets. This allows, as observed, platelets to have 3-, 4-, 5-, and 6-sided edges, hence, multiple tilings. A model for a lattice structure of the organic matrix is forwarded that satisfies all the experimentally observed crystallographic and space filling requirements for longitudinal and transverse directions.

Possible implications of these results on the macrostructure of the nacre in three different species of mollusks will be discussed in reference to *Pinctada margaritifera* and *Nautilus pompilius*, as well as *Haliotis rufescens*. Finally, these results show that by studying the hard tissues it may be possible to discern the structure of the organic matrix in these and other biological composites.

THE FUNCTIONS OF BIOCOMPOSITES

Stephen A. Wainwright

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Duke University
Durham, NC 27706 USA

The exciting and important reason why we want new materials is to make new structures and machines. This workshop is based on our having made the decision to take some instruction and inspiration for new synthetic materials from the structure and properties and synthesis of biomaterials. My pitch is that we should be similarly instructed and inspired by the higher level functions of the materials as they occur in plants and animals.

The fibrous nature of biocomposites will be discussed. A fiber may be a single linear polymer molecule or it may be a pack of such molecules bound together or it may be a bundle of such packs. The fiber, pack (spider web silk), or bundle (tendon) may stand alone or it may be twisted into a rope, be in an oriented array in a membrane (shark skin), or be part of a complexly shaped three-dimensional item (whale blubber, intervertebral disc).

In terms of the functional role played by fibrous materials at a higher level, engineers know that a pressurized cylinder can be effectively reinforced against aneurysm by being wound with high modulus fibers at a helical angle of 55° to the cylinder's long axis. Most engineers are unaware that this material structure in the cylinder wall material also allows the cylinder to undergo bending without kinking, and that this ability is proportional to the pressure in the cylinder. A view of this higher level function could cause a designer to alter the helical fiber angle in the material. Plant cells, worms, fish, whales, and arteries share this material feature and system properties. Bending without kinking helps keep the efficiency of flow through cells and arteries and around bodies (worms and fish) high.

**MICROSTRUCTURE-PROPERTY RELATIONS
IN VERTEBRATE HARD TISSUES:
MICRODAMAGE AND TOUGHNESS**

John D. Currey

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York, YO1 5DD ENGLAND**

Vertebrate hard tissues have a mineral content varying from about 50% V/V to 98% V/V, producing considerable variation in Young's modulus (4-35 GPa). Variation in toughness, measured by work of fracture, is much greater (20-6,000 J-m⁻²). This variation is partially a function of mineral content (highly mineralized tissue being less tough) but is greatly affected by microstructure. Some highly structured, highly mineralized tissues, like enamel, have a plywood-type structure and are rather tough, while ear bones, also highly mineralized, are unstructured and totally brittle.

Similarly, "ordinary" bone may show different toughnesses for any particular amount of mineralization; these differences must be caused by microstructural differences. Bone and dentine undergo considerable generalized microcracking before dangerous travelling cracks appear. The mechanism by which these microcracks are interrupted is unknown, as is the detailed distribution and orientation of the cracks in relation to the microstructure. Fractal analysis of fracture surfaces shows clear differences in the *scale* at which the failure fracture surface becomes rather smooth. Such analyses should give insight into processes going on deep in the specimen before failure occurs.

There is almost a step change in the amount of strain that vertebrate hard tissues can undergo before they become damaged at all: less well-mineralized tissues undergoing a strain of > 1% before being damaged, more highly mineralized tissues being damaged at < 0.05%. Furthermore there is evidence that less well-mineralized tissues have some self-healing ability, so that their characteristic increasing compliance with increasing strain is totally reversible. The micromechanism bringing this about is obscure, but it does not seem to be a viscoelastic effect.

STRUCTURES AND PROPERTIES OF BIOLOGICAL MATERIALS

Georgio Jeronimidis^{*} and Julian F. V. Vincent[†]

Departments of ^{*}Engineering and [†]Pure and Applied Zoology
University of Reading
Whiteknights
Reading RG6 2AY ENGLAND

Most biological structures are fibrous composites. The fibers are either polypeptide (e.g., collagen) or polysaccharide (e.g., chitin in insects, the related cellulose in most plants). The strength and stiffness of these fibers are not intrinsically exceptional, although they are near the top end of mechanical performance. What is unique in biological composites is the variety of intermediate structures and morphologies obtained using these fibers and the smooth integration and progression from chemistry to engineering. All biological composites are materials designed for specific, often multiple, functions. The structural level at which specific morphologies and interactions are introduced in the design may vary in different organisms, but the potential for change under varying external factors is always present. This adaptability of biological materials is of great importance for survival and optimization of energetic resources. It is perhaps this last aspect which is important to understand in order to contemplate the development of advanced materials based on biomimicry. The right chemistry and the right components are only the first step. The function or functions and all the structural compromises which will be necessary to accept are the important clues to look at in biology. This requires understanding of both the biological and the materials science aspects.

For some years we have been following essentially this line of thought and will illustrate the ideas with examples culled from both published and unpublished work. We shall discuss the design of a variety of fibrous materials and structures including wood; the flowering stem of the dandelion; other plants (mainly grasses); and various bits of cuticle, keratins, and skins. We shall emphasize the methods for learning principles from these systems and how those principles can be applied to manmade materials.

ROLE OF MOLECULAR GENETICS IN POLYMER MATERIALS SCIENCE

Maurille J. Fournier,*[‡] Thomas L. Mason,*[‡] and David A. Tirrell[†][‡]

Departments of *Biochemistry and †Polymer Science and Engineering, and
‡Program in Molecular and Cellular Biology
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In principle a broad assortment of new and important protein-based materials can be developed by genetic engineering. In this context it should be possible to produce artificial proteins with novel physical and chemical properties by creative joining of structural motifs that do occur in natural proteins, such as α -helices, β -sheets and β -turns. Especially noteworthy is the fact that biological synthesis offers better control over polymer chain architecture than is possible by current chemical methods, including control of molecular size, sequence, and stereochemistry. Our group is producing recombinant protein polymers designed to form crystalline chain-folded lamellar structures of defined thickness and surface function. These materials feature repeating stem-turn elements composed of β -strands and amino acids predicted to participate in β -hairpin formation. The resulting β -pleated sheets are expected to associate through intersheet packing. The polypeptides of present interest have the sequence $-[(\text{GlyAla})_3\text{L}_1\text{L}_2]_n-$, where GlyAla dyads form β -strands, and residues L_1 and L_2 allow β -turn formation. The protein products are encoded in chemically synthesized DNA and produced in recombinant bacteria, in particular *Escherichia coli*.

The biological feasibility of our approach has been demonstrated for several synthetic genes. The DNA coding units are genetically stable and the artificial genes are expressed with good efficiency to yield apparently monodisperse proteins of expected size and composition. Thus far, one protein of sequence $[(\text{AlaGly})_3\text{GluGly}]$ has been shown by x-ray diffraction analysis to form highly ordered crystalline material. Presently we are studying: (i) the effects of amino acid sequence on β -turn formation, (ii) the influence of stem length and amino acid composition on chain folding and materials properties, and (iii) the potential for biological incorporation of unnatural amino acids into the product proteins, to expand the chemical and physical properties available with the 20 natural amino acids. Several proteins with different two-amino-acid-turn sequences have been successfully expressed and a protein believed to contain selenomethionine at putative turn sites has been produced. Our strategies for designing and producing recombinant protein materials will be presented and the properties and potential applications of the resulting products will be discussed.

Contributing colleagues in our laboratories include: Kevin McGrath, Mark Krejchi, Michael Dougherty, Howard Creel, Ted Atkins (Univ. Bristol) and Srinivas Kothakota.

MOLECULAR DESIGN OF SPIDERS' SILKS

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Spiders produce a variety of high-performance, tensile fibers (silks) by spinning from concentrated, aqueous protein solutions. Recent developments in genetic engineering suggest that the synthesis of novel structural proteins in microbial culture to produce polymers for fibers may become commercially viable in the future. We believe that information about the structure-property relationships of spider silks, as well as an understanding of the methods employed by spiders to process protein solutions into fibers, may provide important guidance for these developments.

At the molecular level, most silks employ microcrystalline structures, based on β -pleated sheet secondary structures, to link polymer chains into a molecular network. The crystals are stabilized by hydrogen bonds between the amide linkages (i.e., peptide groups) in the protein backbone, and in this respect silks are very much like nylons. Alignment of crystal domains is achieved by spinning and by drawing during fiber formation. Thus, many silks exhibit the high stiffness, strength, and toughness characteristic of drawn nylons. In addition, silks contain sequence blocks that do not form crystalline substructures readily, and thus, the molecular network can contain substantial regions of amorphous structure. Finally, because proteins are generally much more polar than nylon, silks are often readily hydrated by water. This means that silks may exhibit elastomeric behavior based on conformational entropy changes if the amorphous polymer segments between crosslinking crystal blocks become kinetically free with hydration.

We have been studying the structure-property relationships of the frame and the viscid silks from the orb web of the spider *Araneus diadematus*. The frame silk represents a high stiffness fiber, with an initial tensile modulus of 10 GPa and a strength of about 1 GPa, whereas the viscid silk is elastomeric, with an initial stiffness of 3 MPa and an extension to fracture of about 300%. Interestingly, both silks have very similar amino acid compositions, so these differences likely represent either major differences in monomer sequence or radical differences in fiber formation. Our studies of these silks have revealed that the potential for crystallization in these two silks is very similar, but that the viscid silk contains a nonvolatile, water soluble component that substantially inhibits crystallization during fiber formation. This component(s) may provide a useful tool for controlling protein crystallization during the commercial spinning of proteins into fibers.

**BIOMINERALIZATION,
THE INORGANIC-ORGANIC INTERFACE
AND CRYSTAL ENGINEERING**

**Stephen Mann, Brigid R. Heywood, Jon M. Didymus, Fiona C. Meldrum,
Sundara Rajam, and Vanessa J. Wade**

**School of Chemistry
University of Bath
Bath BA2 7AY ENGLAND**

The study of biomineralization and related model systems has advanced to a level where major insights in materials science can be expected in the near future. The application of principles such as molecular recognition and self-assembly in the regulation of nucleation and growth is pivotal to a new perspective in the fabrication of advanced inorganic materials. Nanophase and composite materials are immediate candidates for biomimicry. This paper summarizes the main features of biomineralization placing particular emphasis on the importance of specific molecular interactions at interfaces comprising inorganic and organic surfaces. Two examples are described: (i) structural studies on the oriented nucleation and growth of calcite (CaCO_3) crystals in the coccolith plates of marine algae and (ii) iron oxide mineralization in site-directed mutants of the iron storage protein, ferritin. Recent studies of model systems of biomineralization are also discussed. One approach is based on the integration of supramolecular chemistry into materials science. Experiments involving the use of (i) vesicles and protein micelles in the controlled formation of inorganic materials of nanometer dimension and (ii) Langmuir monolayers as organized molecular templates for oriented nucleation are reviewed. A second approach involves the engineering of crystal shape through the design of low molecular weight organic additives. The geometric, electrostatic, and stereochemical factors responsible for crystal chemical specificity in these model systems are discussed.

CRYSTAL ORGANIZATION IN RAT BONE LAMELLAE

Stephen Weiner and Wolfie Traub*

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Rehovot, 76100 ISRAEL

The organization of the mineral crystals in bone has never been established. It is, however, well known that the crystals are intimately associated with the collagen fibrils, and that the collagen fibrils are arranged in parallel arrays in individual bone lamellae. The fibrils in alternating lamellae have different orientations, such that they form a plywood-like structure. A scanning electron microscope (SEM) study of the fracture surfaces of the midshaft of rat tibia reveals a well-developed cleavage pattern, with the main cleavage planes oblique to the lamellar boundaries. A transmission electron microscope (TEM) study of small crushed bone particles shows that the plate-shaped crystals are arranged in parallel layers, as has been described for the organizational motif of crystals in mineralized turkey tendons.¹ Large bone particles tend to show crystal layers oriented in one direction in one part of the particle and in a different direction in another. Electron diffraction patterns from the two different parts show that the crystal *c* axes have two different orientations. As crystal *c* axes are well aligned with collagen fibril axes, this implies that the fibrils in the two areas have different orientations, or in other words, the particle is composed of portions of two adjacent lamellae. Combining the SEM and TEM observations, and assuming that the cleavage planes observed in the SEM correspond to crystal layers, we conclude that the basic organizational motif of rat bone lamellae is one in which the crystals are arranged in parallel layers in individual lamellae, but that the orientations of these layers in alternate lamellae are different. We refer to this structure as "rotated plywood."

1. W. Traub, T. Arad, and S. Weiner, *Proc. Natl. Acad. Sci. USA*, **86**, 9822-9826 (1989).

COMPOSITE MATERIALS COMPOSED OF SINGLE CRYSTALS AND PROTEINS: COMPARISON BETWEEN MOLLUSK PRISMATIC LAYER AND SEA URCHIN SKELETONS

Amir Berman,* Lia Addadi,[†] and Stephen Weiner*

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Single crystals are attractive materials because of their order, close packing, and intrinsic physical properties. Mechanically, single crystals may have disadvantages due to anisotropic growth and the presence of well-developed cleavage planes. Organisms have found complex and elegant solutions to these problems, in part through interactions of growing crystals with specialized acidic proteins. These macromolecules appear to be able, in different systems, to induce crystal nucleation, modulate crystal growth, and influence the properties of the single crystals. In sea urchin skeletons, whole macroscopic plates and spines are single calcite crystals, but fracture as amorphous materials. Acidic proteins are intercalated inside the single crystals by adsorption, during growth, on specific crystal planes. Their presence inside the lattice interferes with the propagation of fracture along the cleavage planes, thus mechanically reinforcing the crystal: a new concept of composite material.¹ In the mollusk shell prismatic layer, the design principle is based on the growth of oriented calcite crystal arrays inside a preformed organic matrix. Acidic proteins are present, but do not affect single crystal properties in a manner analogous to the sea urchin. They inhibit growth and possibly induce oriented calcite crystal nucleation but, although some are occluded inside the crystals, they do not interfere with cleavage. A comparison of the properties of these materials has been performed at the level of single crystals, on both synthetic and biogenic specimens. This includes crystal nucleation and growth experiments and synchrotron x-ray studies of crystal texture.² The sea urchin proteins show controlled intercalation at the boundaries of large perfect crystal domains, whereas the mollusk shell proteins appear to be only nonspecifically occluded into calcite. The generality of these effects and their applicability to artificial systems are presently under investigation.

1. A. Berman, L. Addadi and S. Weiner, *Nature*, **331**, 546-548 (1988).

2. A. Berman, L. Addadi, A. Kvick, L. Leiserowitz, M. Nelson, and S. Weiner, *Science*, **250**, 664-667 (1990).

ULTRAFINE INORGANIC PARTICLE FORMATION IN BACTERIA

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Bacteria produce intracytoplasmic, submicron inorganic particles in connection with their metabolic and magnetotactic activities. Some bacteria deposit iron in the form of an amorphous, hydrous-ferric-phosphate in storage proteins, the bacterial ferritins. Magnetotactic bacteria produce single-magnetic-domain-size particles of ferrimagnetic magnetite (Fe_3O_4) or greigite (Fe_3S_4), which are responsible for the magnetotactic response. In some organisms, nonmagnetic particles of pyrite (FeS_2) are also found. The iron-oxide and iron-sulfide particles have species-specific morphologies, which implies a high degree of control by the organisms over the biomineralization process. Gorby et al. have shown that in the magnetotactic bacterium *A. magnetotacticum* magnetite particles are deposited within the cytoplasmic membrane. There is evidence for an encapsulating membrane for inorganic particles in other magnetotactic bacteria as well. This membrane is presumably the locus of control by these organisms in biomineralization.

SIZE-QUANTIZED PARTICLES AT ARTIFICIAL MEMBRANE INTERFACES

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Infusion of H_2S onto cadmium and zinc arachidate monolayers resulted in the formation of size-quantized CdS and ZnS particles which could be transferred, essentially intact, to solid substrates at different stages of their growth. Reflectivity, absorption, spectrophotometry, transmission electron microscopy, and x-ray diffraction measurements established the presence of porous semiconductor particulate films. Scanning tunneling microscopy (STM) allowed the observation of the earliest stages of particle growth. The initially formed microclusters, as small as 5 Å in diameter, aligned themselves and grew laterally to linked, 50-150 Å in diameter, 20-30 Å thick, disk-shaped polyparticles. With continued H_2S infusion, these polyparticles formed an interconnected semiconductor particulate film whose thickness grew to a limiting value.

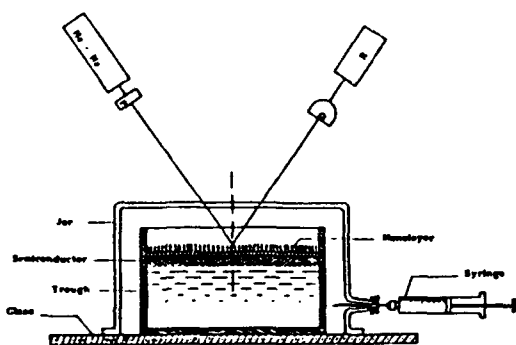


Fig. 1. Schematics of the experimental arrangement used for the generation of semiconductor particles.

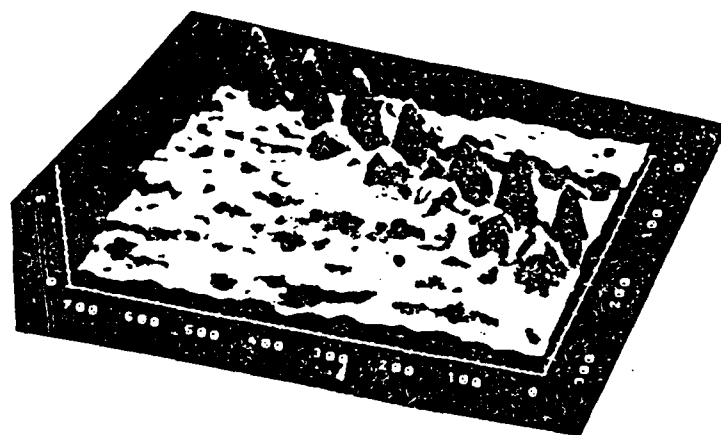


Fig. 2. STM microscopic images on highly oriented pyrolytic graphite of ZnS particles, *in situ* formed on zinc arachidate monolayers.

**HIERARCHICAL STRUCTURES OF SOFT CONNECTIVE
TISSUES – RELATIONSHIPS TO PROPERTIES AND FUNCTION**

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Hierarchical structures in biocomposite systems such as in collagenous connective tissue have many scales or levels, have highly specific interactions between these levels, and have the architecture to accommodate a complex spectrum of property requirements. As examples, the hierarchical structure-property relationships will be described in three soft connective tissues: tendon, intestine, and intervertebral disc. In all instances, we observed numerous levels of organization with highly specific interconnectivity and with unique architectures that are designed to give the required spectrum of properties for each oriented composite system. From these lessons in biology, the laws of complex composite systems for functional macromolecular assemblies will be considered. Finally, demonstrations will be given on the application of these laws to simple synthetic composites, including continuous multilayered polymeric materials, liquid crystalline polymers, and "hard elastic" membranes. Again, it will be shown that structure-property relationships can only be described, and in some instances predicted, if these complex synthetic materials are accurately defined in terms of their hierarchical structure.

THIN FILM BIOMIMETIC COMPOSITES AND CERAMICS

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The examples of shell, bone, and tooth tell us that it is possible to make composite materials by deposition of reinforcing particles into macromolecular matrices. We should be able to achieve particle packing densities up to 95% by volume, high levels of particle orientation, and very fine particle sizes. What we have to do is learn how. It is clear that biological mechanisms controlling mineralization are very complex, but such complexity may not be necessary to produce a good material.

Our work has focused on the precipitation of oxide particles by hydrolysis of alkoxides entrained within a polymer. We have demonstrated that this method does form films containing up to 30 vol% of 1 micron particles, and that these films can be sintered to make a ceramic. Recent studies have focused on the reaction mechanisms and methods of increasing the level of control which the matrix can exert on the precipitation.

We will also try to address the question of what we mean by biomimetic processing in terms of the approaches to be used and the materials goals which we hope to reach.

PROCESSING OF CERAMICS BY BIOMIMICKING[†]

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In this presentation we will illustrate the feasibility of utilizing biomimetic processing procedures in the processing of materials. Four specific examples will be illustrated: (i) the use of biopolymers as dispersants in the colloidal processing of ceramics; (ii) synthesis of nanometer-sized, multicomponent particles with phospholipid vesicles; (iii) processing of laminated ceramic-metal and ceramic-polymer composites as analogs of mollusk shell; and (iv) the modification of wood properties through partial mineralization.

In the first area, we will illustrate that rheological properties of ceramic particle-containing suspensions can be modified by growing the alginate-producing bacterium, *Azotobacter vinelandii* directly in the presence of aluminum oxide particles. Mechanisms leading to suspension stabilization will be discussed with respect to the role played by polymannuronic and polyguluronic acid components of the alginate. The most important aspect of these findings is that unlike the processing schemes used in most applications, the use of water-based biopolymers may provide an opportunity to process ceramics by ecologically balanced processing procedures.

In the second area, our examples will build onto the pioneering works of Janos Fendler and Stephen Mann on the formation of nanometer-sized particles in vesicles. As a follow-up to their studies, we will highlight the advantages of vesicle-mediated particle processing and consolidation in nanocomposite processing. Particular emphasis will be on the lubricating properties of bilayers.

In the third area, we will illustrate the advantages of mimicking mollusk nacre structure as laminated B₄C-Al and ceramic-polymer composites. In comparison to methods used in biological systems, although our mimicking approaches are very crude, the improvements in properties are significant enough to warrant further research in this area.

The last illustration will be on the modification of wood properties through the formation of ceramics (SiO₂ and/or AlOOH) in the cell walls and cells.

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